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Fabrication and Pilot Scale Testing of a Prototype Donnan Dialyzer for the Removal of Toxic Metals from Electroplating Rinse Waters

Southwest Research Inst., San Antonio, TX

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16. ABSTRACT

This report concerns research performed to develop anion-exchange membranes for the removal of copper, cadmium, and zinc, as their complex cyanide anions, from cyanide process electroplating rinse waters by Donnan dialysis, and to fabricate and evaluate a prototype Donnan dialyzer ultilizing these membranes. Results obtained from this study indicate that anion-exchange membranes with transport properties suitable for the removal of metal complex anions can be prepared by irradiation grafting of polymer films. Evaluation of these membranes showed that ion transport rates are directly proportional to ion-exchange capacity. A series of technical problems with ion-exchange membrane preparation and with operation of the prototype dialyzer precluded successful completion of the follow-on project.

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EPA Cooperative Agreements CR 807476 and CR 809761

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's research and development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges, establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution, and assessing the nature and controllability of releases of toxic substances to the air, water and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report concerns research performed to develop anion-exchange membranes for the removal of copper, cadmium, and zinc, as their complex cyanide anions, from cyanide process electroplating rinse waters by Donnan dialysis, and to fabricate and evaluate a prototype Donnan dialyzer utilizing these membranes. Results obtained from this study indicate that anion-exchange membranes with transport properties suitable for the removal of metal complex anions can be prepared by irradiation grafting of polymer films. Evaluation of these membranes showed that ion transport rates are directly proportional to ion-exchange capacity. A series of technical problems with ion-exchange membrane preparation and with operation of the prototype dialyzer precluded successful completion of the follow-on project.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

A program was conducted to develop anion-exchange membranes to be used in the removal of copper, cadmium, and zinc, as their complex cyanide anions, from cyanide process electroplating rinse waters by a Donnan dialysis process. For these laboratory studies, simulated rinse waters prepared by diluting electroplating bath solutions to the desired metal content were utilized.

A series of anion-exchange membranes based on radiation grafted polyethylene films were prepared. The grafting monomers used were vinylpyridines or vinylbenzyl chloride. These grafted membranes were converted to anion-exchange membranes by quaternization with alkyl halides or trialkylamines, respectively. The series of membranes exhibited varying ion-exchange capacities and varying hydrophilicity.

Evaluation of the membranes in Donnan dialysis showed that ion transport rates are directly proportional to ion-exchange capacity. Previous studies have shown that the effect of membrane hydrophilicity is more complex; very low hydrophilicity leads to zero ion transport. Moderate hydrophilicity gives membranes with good transport properties. Very high hydrophilicity leads to membranes with very low ion selectivity, as cation leakage becomes excessive and reduces the potential for anion selective transport.

A follow-on program was conducted to fabricate a prototype Donnan dialyzer to be used for the removal of copper, cadmium and zinc, as their complex cyanide anions, from cyanide process electroplating rinse waters. The prototype dialyzer was to be evaluated in actual electroplating shops in order to obtain data allowing engineering and economic analysis of the suitability of Donnan dialysis as a pollution control technology for this application.

The prototype dialyzer was to utilize membranes developed in the above study. Synthesis of the required quantity of membranes for the dialyzer produced a product membrane which was unstable in the dialyzer stripping solution. Attempts to resolve the instability problem were unsuccessful. Alternate membranes produced by Southwest Research Institute (SwRI) and three commercial membranes were evaluated, and an SwRI membrane was selected for use in the prototype dialyzer. The dialyzer was fabricated and laboratory tests were carried out prior to field evaluation. A series of technical problems were encountered with the plate and frame hardware for the dialyzer. The most serious involved development of internal leaks between the rinse water and stripping solution. These problems indicated that a major redesign of the dialyzer was required. After consideration of financial and time requirements for the redesign effort, a decision was made to terminate the program.

This report was submitted in fulfillment of Cooperative Agreements CR 807476 and CR 809761 by Southwest Research Institute under partial sponsorship of the U.S. Environmental Protection Agency and the American Electroplaters Society. This report covers the program periods April 1980 to March 1982 and February 1982 to November 1984.

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SECTION 1

INTRODUCTION

In the past several years, legislation has been passed at state and federal levels leading to the limiting of allowable emissions of many trace metals in water from industrial sites. Among the metals are copper, zinc, nickel, chromium, cadmium, lead and mercury. Removal of these metals, present as ions, from the untreated industrial outflows will therefore be required. In certain cases, the removal may take place by using various means such as reverse osmosis, dialysis and electrodialysis. All of these methods have certain advantages and disadvantages.

One method of removal of trace metals from aqueous effluents, which has been applied with success in recent years, is the use of ion-exchange resins. An approach which incorporates the advantages of ion-exchange systems is a membrane transfer process known as Donnan dialysis. This process is basically a continuous ion-exchange procedure utilizing an ion-selective membrane. This process utilizes the permselective properties of the ion-exchange membrane to establish a Donnan equilibrium (1) between the two solutions of electrolytes separated by the membrane. In the case of an anion-exchange membrane, the cations in the two solutions are prevented from interdiffusing across the membrane, but the anions will redistribute themselves between the two solutions until equilibrium is reached and the ratios of all similarly charged anions are equal. The driving force for anion exchange is the system's displacement from the equilibrium ratios and can be controlled by manipulation of the solution concentrations. When the concentration of one anion is substantially higher in, say, the left side of the cell, the cation concentrations in the two solutions are maintained due to the impermeability of the membrane for cations. However, there is a net effect of diffusion of any other anions from the right side of the cell, to the left side of the cell across the membrane, and against the concentration gradient where they reach a concentration many times that in the original solution in the right side of the cell. They are replaced in the right side of the cell by counterdiffusion of the added anions in the left side of the cell. A more detailed discussion of Donnan dialysis is given in Section 5 of this report.

The simplest Donnan dialysis cell comprises an ion-selective membrane and a spacer on each side of the membrane. The toxic heavy metal ions in a rinse water feed can be extracted across the membrane and concentrated in a stripping solution. The only energy required in such a process is to pump the feed and stripping solutions across the cell. Large hydraulic pressures as required by reverse osmosis or large electric current flows as required by electrodialysis are not required in Donnan dialysis. A compact Donnan dialysis stack can be designed to contain many membrane-spacer units to economically treat large quantities of rinse water.

The E. I. duPont de Nemours Company presently markets "Nafion," a perfluorosulfonic acid membrane which is being evaluated in Donnan dialysis for recovering metal ions such as cesium-137, mercury and strontium. The presently available material is quite expensive, selling at about $322 per square meter ($30 per square foot), and the feasibility of using the membrane in commercial Donnan dialysis applications has not been fully established. Nafion films have also been investigated for the removal of nickel in electroplating rinse water (2). Research showed that nickel could be removed from rinse water at a rate of approximately 21 $g/hr/m^2$ (0.004 $lb/hr/ft^2$) membrane when utilizing rinse water containing about 500 ppm nickel at a feed rate of approximately 7.61 Lpm (2 gpm).

Of particular interest at present, this technique is being extended to the removal of other trace metals from electroplating wastes. Cadmium, copper, and zinc are important as they are present in electroplating wastes as their complex cyanide anions. Removal of these trace metals will therefore require the development of suitable anion-exchange membranes, in contrast to the removal of nickel which is present as its free cation and could thus be removed with cation-exchange membranes. Conventional rinse water treatment involves chlorination for cyanide destruction, followed by precipitation of the metals as their hydroxides or sulfides. Donnan dialysis, provided high transport membranes are available, could provide a simple, efficient alternative electroplating rinse water treatment process.

The objective of the initial study was the development of optimized anion-exchange membranes for the removal of copper, zinc and cadmium, as their complex cyanide anions, from electroplating rinse waters. During the course of this laboratory study, all membrane evaluations were conducted with simulated electroplating rinse waters. These were prepared by diluting plating bath formulations to give the desired metal ion concentration (50 ppm or 500 ppm).

The objective of the follow-on study was the fabrication and evaluation of a prototype Donnan dialyzer for the removal of copper, zinc and cadmium, as their complex cyanide anions, from cyanide process rinse water. The field evaluation of the dialyzer in electroplating shops was intended to provide engineering data to allow technical and economic analysis of Donnan dialysis as a means of removing toxic metals from electroplating rinse waters.

SECTION 2

CONCLUSIONS

The results obtained in the initial study indicated that anion-exchange membranes with transport properties suitable for removal of metal complex anions from electroplating rinse waters by Donnan dialysis can be prepared by irradiation grafting of polymer films.

The results further indicate that membranes prepared by grafting with 4-vinylpyridine followed by quaternization with methyl iodide are superior to membranes prepared by grafting with vinylbenzyl chloride followed by quaternization with trimethylamine.

The data show that the ion transport rates across the membrane are proportional to membrane ion-exchange capacity, i.e., the higher the ion-exchange capacity, the higher the transport rate. However, equilibrium water content also increases the increasing ion-exchange capacity.

Previous work (4) has shown that increased membrane hydrophilicity can lead to decreased transport rates. If a membrane absorbs large volumes of water, the charge density within the membrane is decreased due to the large wet volume of the membrane. This reduced charge density leads to a decrease in the Donnan potential across the membrane and results in reduced ion transport rates.

Two major technical problems were encountered in the course of the follow-on program. The first involved the inability to reproduce the synthesis of the high transport rate membrane developed in the initial study. All attempts to prepare this membrane led to a product which was unstable in the basic stripping solution. The problem of the membrane stability was not resolved. Therefore, it was necessary to use membranes with lower transport rates in the dialyzer fabrication.

The second problem encountered involved the development of internal leaks in the dialysis unit. The exact cause of these internal leaks could not be ascertained but probably was due to insufficient support for membranes under the applied hydraulic loads resulting in damage to the membranes.

As a result of these problems, no field evaluation data on metals removal from electroplating rinse waters were obtained. Therefore, no technical or economic evaluation of Donnan dialysis for this application can be made.

SECTION 3

RECOMMENDATIONS

The data obtained in the initial study indicate that the best membranes prepared in this study show acceptable performance for removal of metal-cyanide complex anions from simulated electroplating rinse waters under laboratory conditions.

It is recommended that further studies be conducted to evaluate the most promising membranes under field conditions. The recommended field study would entail preparation of sufficient quantities (37.2 to 74.4 m^2, 400 to 800 ft^2) of Membrane E11Q4 to construct a prototype Donnan dialyzer capable of treating rinse water streams containing about 500 mg/L levels of metal ions at flow rates of 11.4 to 19 L/min (3 to 5 gpm).

A thin flow channel (1 mm, 0.044 in.) dialyzer containing 75 m^2 of Membrane E11Q4 (transport rate constant 1.5 min^{-1}) is calculated to give a metal removal of 99.8% with a feed rate of 19 L/min and 500 ppm metal in the feed.

The prototype dialyzer could be evaluated on electroplating rinse waters in commercial plating shops to obtain engineering data. These data would allow technical and economic evaluation of Donnan dialysis as a means of controlling effluent levels of copper, cadmium and zinc from commercial plating lines. It would also provide field experience on membrane life and maintenance. Quantities of spent stripping solution would be available for characterization and study as to the best means of disposal.

The results of the follow-on study did not allow the technical or economic evaluation of Donnan dialysis as a pollution control device in electroplating shops.

The lack of success of this program is attributable to inability to reproduce the synthesis of high transport rate membranes and to mechanical problems with the dialysis unit. The dialyzer problems were probably due in part to the complexity of the dialyzer design.

Any future work in this area would benefit from careful consideration of dialyzer design. Tube- and shell-type units (2), fabricated from bundles of small diameter ion-exchange tubing sealed into a tubular housing at the ends, would minimize seal problems. Procedures for isolating leaks within individual ion-exchange tubes followed by plugging of any leaking tubes could provide a relatively simple and easy means of eliminating internal leaks. Finally, the technology for preparing ion-exchange tubular membranes by irradiation-initiated grafting of small diameter, thin wall polyolefin tubing exists and could be readily optimized. This approach should provide a dialyzer which is more easily constructed and maintained and is less susceptible to internal leaks. Consideration of a system of this type is recommended for consideration in any future program in this area.

SECTION 4

EXPERIMENTAL PROCEDURES

FILM GRAFTING PROCEDURES

Procedure for Irradiation Grafting of Polyethylene Film

Polyethylene film (0.025 mm thick, 36.6 cm wide) was backed with cheesecloth and rolled onto a 12.7-mm aluminum rod. In screening runs, the length of film used was 1.52 m. Longer lengths (7.62 m) were prepared of films that showed promise to provide larger quantities of film for evaluation. Production runs utilized 30.5 m lengths of film.

The roll of film and backing material were placed in a suitable size hydrometer jar (38 mm x 357 mm for 1.52-m rolls; 75 mm x 550 mm for 7.62-m rolls). For the small rolls, the aluminum pipe was removed prior to placing in the jar, while the pipe was left in the larger rolls. The hydrometer jar was then closed with a rubber stopper fitted with inlet and outlet tubes that were sealed with vacuum tubing and screw clamps. For production runs, six rolls of film and backing material were placed into a cylindrical aluminum reactor (33 cm diameter x 76 cm high) and the reactor cover bolted in place. The reactor was connected to a vacuum pump and evacuated to approximately 10 to 12 Torr to remove air. The reactor was then backflushed with nitrogen. The evacuation-nitrogen backflush cycle was repeated six times.

A grafting solution of the desired monomer in a suitable solvent was drawn into the evacuated reactor. During screening runs, the grafting solution usually contained 25% monomer by weight. Solvents used were benzene, methanol, or water, depending upon the solubility properties of the monomer. The filled reactor was alternately evacuated and pressured with nitrogen several times to remove air entrapped in the roll, and inlet and outlet tubes were sealed. The filled reactors were allowed to stand for at least 24 hours to provide time for the film to equilibrate with the grafting solution.

The reactors were placed on turntables in the irradiation facility and were exposed to a uniform cobalt-60 source adjusted to give the desired dose rate. The irradiation was continued until the desired total dose had been applied. The reactors were rotated during the irradiation period in order to apply a uniform radiation dose to the film.

The irradiation tables were constructed so eight samples could be run simultaneously under equivalent conditions with hydrometer jars. Two turntables were used for simultaneous irradiation of two large production reactors.

After completion of the irradiation period, the reactors were removed from the irradiation facility and allowed to stand for 24 hours in order to permit reaction of the remaining active sites.

The film was removed from the reactor, unrolled and separated from the cheesecloth. The film was then washed in solvents suitable for removing homopolymer which was deposited on the film and allowed to dry on paper toweling.

Irradiation Configuration and Dosimetry

Irradiation of the polyethylene rolls was carried out in Southwest Research Institute's radiation effects facility. The radiation source consists of approximately 13,000 curies of high specific activity cobalt-60. The cobalt-60 sources are individually encapsulated in stainless steel right circular cylinders approximately 2.54 cm in diameter. To provide a uniform radiation field wide enough for eight samples and high enough to cover the large rolls, the individual cobalt-60 cylinders were evenly spaced on the center line of a vertical source holder which was mounted on a remote-controlled dolly.

Mapping the gamma flux in the target area (front) of the source indicated workable isodose volumes of 20,000 rad sufficient to contain the turntables and target cylinders. This volume was almost semicircular and symmetrical about the center line of the source, with the center cylinders offset slightly farther from the source.

Detailed dosimetry using the Bausch and Lomb cobalt glass chip dosimeters or lithium fluoride crystal dosimeters was performed on the irradiation tables and large hydrometer jars. The entire assembly was adjusted in position or source strength until it was determined that the incident dose rates were those specified for each of the eight turntable stations, within the error of the dosimetry system. Dosimeters were placed within the cylinders (in air) at the top, middle and bottom volume occupied by the polyethylene rolls and near the inside surface of the cylinder. The dosimeters were wrapped in lead foil to shield them from low energy ''knockout.'' The cylinders were rotating in each case, so the measured dose rate was an average of the small difference in rate across the diameter of each cylinder. The target incidence dose rate was 20,000 rad per hour during dosimetry. Lower dose rates were then obtained by increasing the source-to-target distance. Dosimetry checks at one or two points in the target array were then sufficient, since the irradiation field is symmetrical and uniform.

FILM QUATERNIZATION PROCEDURES

The grafted films prepared in this study utilized 2-vinylpyridine, 4-vinylpyridine or vinylbenzyl chloride as the grafting monomers. It was necessary to conduct a postgrafting reaction to chemically modify the films by introduction of quaternary ammonium groups which provided strong base anion-exchange properties.

The vinylpyridine-grafted films were alkylated with alkyl halides to provide quaternary ammonium halide moieties on the polymer. The vinylbenzyl chloride-grafted films were allowed to react with tertiary amines to provide quaternary ammonium chlorides.

Vinylpyridine films were quaternized with methyl iodide (2% in methanol, 48 hours), with dimethylsulfate (2% in methanol, 48 hours), or with 1-bromobutane (2% in methanol, 48 hours). Vinylbenzyl chloride films were quaternized with trimethylamine (10% in water, 24 hours) or with tri-n-butylamine (10% in methanol, 48 hours).

FILM CHARACTERIZATION

The membranes were characterized for equilibrium water content, ion-exchange capacity, osmotic water transport, and metal complex anion transport. The membranes were pneumatically leak tested.

The equilibrium water content was determined on triplicate samples of each membrane. The sample was equilibrated overnight in deionized water, blotted free of surface water with absorbent paper towels, placed in a tared weighing vial, and the wet weight determined and recorded. The sample was dried to constant weight in a 110°C oven; the dry weight was determined and recorded. The equilibrium water content was calculated as grams of water absorbed per dry gram of membrane. This property is a measure of membrane hydrophilicity. This method is an adaptation of Method 412.1 in Test Manual (Tentative) for Permselective Membranes (3). The total ion-exchange capacity of the membranes was determined according to Section 6 of Method 502.1 in the test manual.

The osmotic water transport rate was determined by placing the membrane in a dialysis cell which consisted of two Plexiglass plates (10.2 cm and 29.2 cm) equipped with inlet and outlet fittings and two flow spacers. The flow spacers were polypropylene mesh with silicone rubber gaskets around the edges. The membrane (exposed area 122 cm^2) was placed between the spacers and end plates, and the entire assembly was clamped together with No. 10 machine screws in holes drilled at 5-cm intervals around the perimeter of the plates. One cell half was connected to a recirculation pump and deionized water reservoir. The other cell half was connected to a recirculation pump and a salt solution reservoir. The salt solution reservoir was calibrated so the volume of liquid could be read to the nearest 0.1 mL. The salt solution concentration was 0.1N NaCl. The recirculation pumps were turned on, and periodic determinations of the increase in the salt solution volume were made. A least-squares straight line was determined for the volume of water transported as a function of time. The slope of this line divided by the membrane area gave the osmotic water transport rate for the membrane under the conditions of the experiment.

The metal complex anion transport rate constants were determined on a laboratory-scale Donnan dialysis system. The initial system consisted of feed and strip solution reservoirs, feed and strip pumps, three dialysis cells in series, and flow meters on the outlets of the last cell to monitor solution flow rates. The cells had an exposed membrane area of 122 cm

(5.1 cm x 24.1 cm) and a flow channel thickness of 0.2 cm which was fixed by the gasket thickness around the edges of the flow spacer. The measured volume of each cell half was 21.6 cm^3. A schematic of the test system is shown in Figure 1. Sample points were located at the feed solution inlet to each cell and at the feed solution outlet of the last cell. The simulated rinse water feed solution was prepared by taking an aliquot of a plating bath solution (plating solution formulations provided by a local plating shop operator) and diluting with water to give either 50 ppm or 500 ppm concentration of the metal of interest. Feed solution volumes were typically 45 L. The sample points consisted of a fitting with a septum, so samples could be withdrawn via hypodermic syringe. The feed solution (simulated rinse water) was pumped through the cells on a once-through basis to waste, and the strip solution was pumped through the system to the strip reservoir for recycle. A run was accomplished as follows. The feed and strip reservoirs were filled with the proper solutions, and the pumps were started. The variable speed pump drives were adjusted to give the desired flow rates. The system was operated for several minutes to allow the flows to stabilize, and the run timer was then started. A sample of the strip solution was taken at time zero. Feed samples were taken at the four sample points (four samples per set) at 4-minute intervals. The run duration was 20 to 30 minutes (four to six sample sets). The timer was stopped and the pumps shut off. A sample of the strip solution was taken. All samples were analyzed for the metal of interest.

Previous work (4) had shown that ion transport in Donnan dialysis obeys first-order kinetics. The first order rate constant k was calculated using the expression

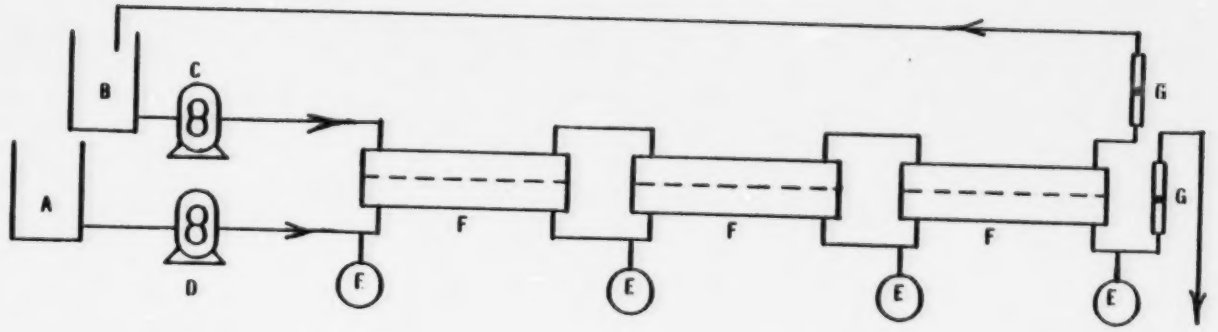
$$k = \frac{\ln \frac{C_o}{C}}{t}$$

where C_o is the concentration of metal ion in the cell inlet, C is the metal concentration in the cell outlet, and t is the residence time in the cell. The calculation for t is

$$t = \frac{\text{cell volume (cc)}}{\text{feed flow rate (cc/min)}}$$

The metal ion transported from the feed was calculated using the flow rate, the run time, and the metal concentration change across all three cells. The metal transferred into the strip was calculated from the metal concentration increase (final concentration minus starting concentration) and the volume of the strip solution. A comparison of these two numbers served as a material balance across the membrane.

Initial membrane evaluations indicated that at flow rates sufficiently high to prevent concentration polarization, the simulated wash water contact time in the cell was too short to give metal complex anion removal rates



A - Feed Reservoir
B - Strip Reservoir
C - Strip Pump
D - Feed Pump

E - Sample Points
F - Test Cells
G - Flow Meters

Figure 1. Membrane test system

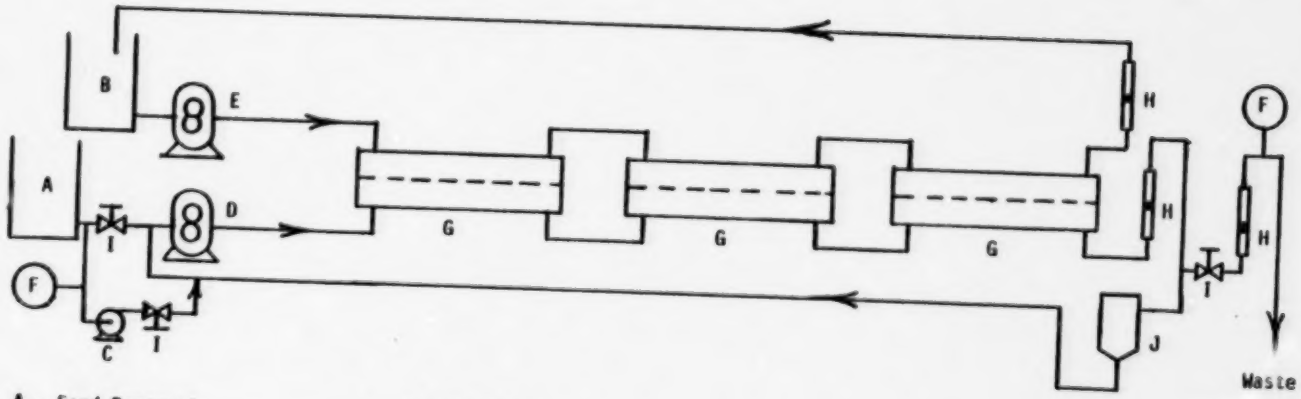
which were capable of being accurately determined. The change in metal ion concentration across the cells was not significantly larger than the expected analytical error, resulting in very imprecise determinations of the metal ion removal rate constants.

The membrane test system was modified to provide high flow rates through the cells by means of an internal recycle loop. It was estimated that cell contact times on the order of 0.5 to 0.7 minutes would be required to give significant metal ion removal. Three cells, each with an effective volume of 21.6 mL, were connected in series for a total effective volume of 64.8 mL. Feed to the system and discharge to waste were controlled at 100 mL per minute to provide a residence time of 0.65 minutes. Flow rate through the cells was maintained at 2 L per minute via internal recycle. A schematic of the modified system is shown in Figure 2. Although the schematic shows a horizontal arrangement, the three dialysis cells were vertically mounted with inlets at the bottom and outlets at the top.

The system was operated as follows. The discharge valve was opened, the inlet valves for the feed and recycle pumps were opened, and the pumps were started. The cells were allowed to fill and while the solution recirculated at 2 L per minute, the transparent cells were observed for the presence of trapped air bubbles. Air bubbles were rapidly carried out of the cells, either due to the velocity of the liquid streams or due to local turbulence promoted by the mesh flow spacer. Air bubbles in the strip solution side of the cells were separated upon discharge at the strip reservoir. Air bubbles in the feed were separated in a glass gas-liquid separator installed in the feed recycle loop. As soon as the system was filled with liquid, the valve between the feed reservoir and the recycle pump was closed. The variable speed drives were adjusted to give a recycle rate of 2 L per minute and a feed rate of 100 mL per minute. The discharge valve was adjusted to give a discharge rate of 100 mL per minute. The strip solution recycle rate was set at greater than 1 L per minute. Periodic samples of feed and effluent were taken. The system was at steady-state when sequential samples of the effluent showed a constant metal content.

Experience with this system showed that even with slow membranes the system reached steady state in under 2 hours. Therefore, the system was filled and operated for 2 hours before initiating sampling. Samples of feed and effluent were then taken at 20-minute intervals for 4 hours (13 sample sets).

The rate constant for metal transfer could then be calculated from the feed concentration, the effluent concentration, and the contact time which was determined by dividing the total effective cell volume (3 x 21.6 mL) by the feed rate. With the modified test system, variable metal ion transport rates were encountered during the initial period of each run until the system came to steady-state conditions. As a result, meaningful material balance calculations could not be made; therefore, stripping solution samples were not taken.



A - Feed Reservoir
B - Strip Reservoir
C - Feed Pump
D - Recycle Pump
E - Strip Pump

F - Sample Points
G - Test Cells
H - Flow Meters
I - Control Valves
J - Gas-Liquid Separator

Figure 2. Modified membrane test system

The sampling procedures and methods of analysis for metal ion concentrations are presented along with quality assurance procedures in Appendix A, Sampling and Analytical Plan.

Prior to evaluation, the membranes were leak tested. Each membrane was placed between cell halves which consisted of Plexiglass plates with gasketed edges. The two cell halves were clamped together with toggle clamps so the membrane formed a barrier between the cell halves. One cell half was connected to a regulated air supply and the other cell half was isolated from the atmosphere with a bubbler. The membrane was placed in the cell and 34.5 KPa (5 psig) air was applied to the cell. After an initial flow of bubbles in the bubbler due to deformation of the membrane under the applied pneumatic load, all gas flow in the bubbler stopped for a leak-free membrane. The continued flow of air through the bubbler indicated a pinhole leak in the membrane.

PROTOTYPE DIALYZER DESIGN

The prototype Donnan dialyzer was a plate and frame design modeled upon a unit described by David, Wu and Baker (5). The dialysis stack design called for a total of 75 membranes arranged to give parallel flow. Each membrane was 35.6 by 96.5 cm and had an active area of 0.279 m^2. Total active membrane area in the dialyzer was 20.92 m^2.

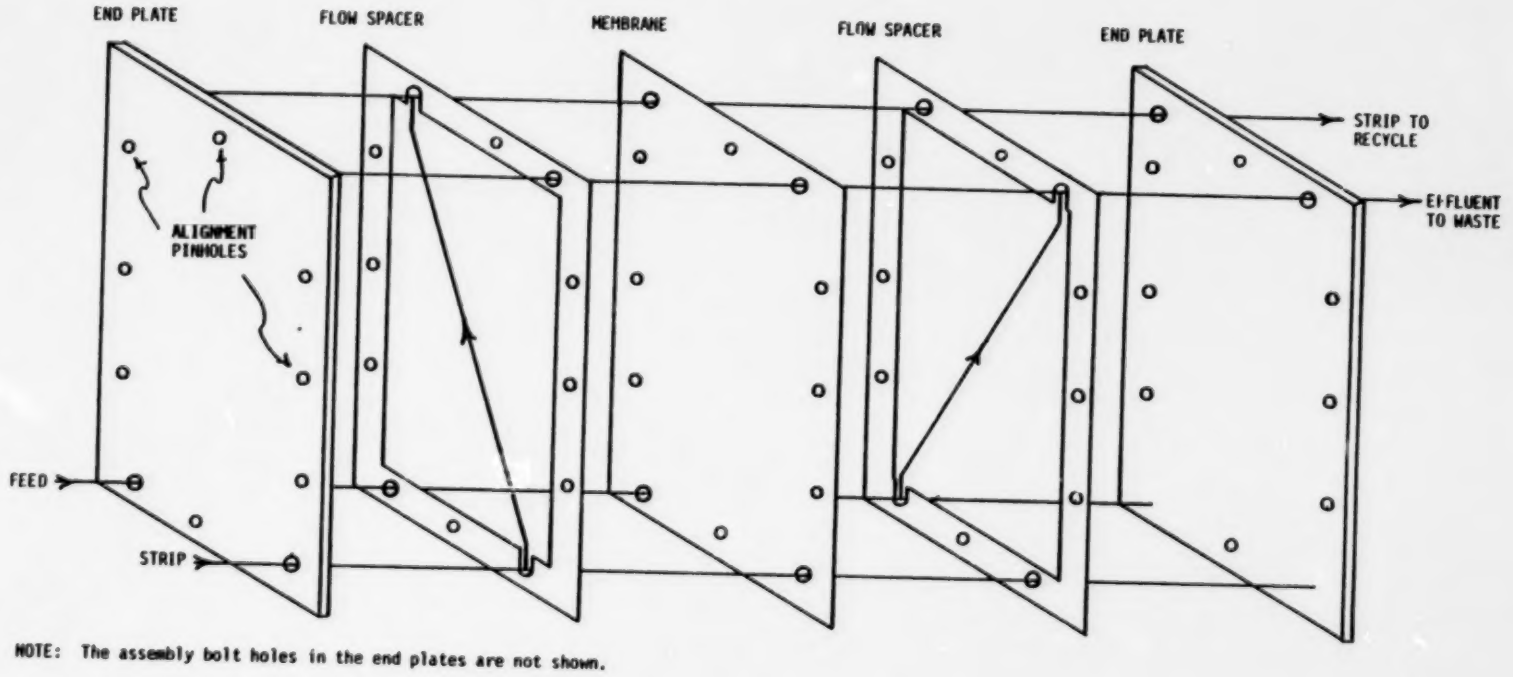
Flow spacers were fabricated using polypropylene mesh (0.5 mm x 40.6 cm x 101.6 cm). The border (5.08 cm) of each spacer was impregnated with a room temperature vulcanizing silicone rubber and the border was faced on each side with neoprene rubber gaskets (5.08 cm wide x 0.9 mm thick) to provide a three-layer laminated gasket integral with the mesh flow spacer. The open area of each spacer was 30.5 cm x 91.5 cm (0.279 m^2). Entry and exit ports were cut in the gaskets so upon assembly in the dialysis stack inlet and outlet manifolds for the wash water and stripping solution were formed. The individually leak-tested membranes were cemented to the flow spacers with a liquid rubber adhesive.

The dialysis stack end plates were fabricated from aluminum plate (2.54 cm x 44.5 cm x 104.1 cm). Four locating pins (9.5 mm diameter x 25 cm length) were screwed into threaded holes in the top, bottom and side edges of one plate. Matching holes were drilled in the other end plate. The locating pins were situated so they passed through holes in the flow spacer gaskets thus providing proper alignment of the end plates and membrane-flow spacer assemblies. Inlet and outlet ports were drilled in the end plates in alignment with the inlet and outlet manifolds in the gasket assemblies and were fitted with 12.7-mm compression fittings. It was subsequently found necesasry to incorporate additional locating pins (two additional per side) on the long sides of the end plates to provide increased lateral support for the membrane-spacer assemblies.

The dialyzer was assembled by stacking the 75 membrane-spacer assemblies on the locating pins on one end plate via holes cut in the center line of the gaskets and placing the other end plate over the locating pins.

the end plates were then secured with 26 bolts (9.5 mm diameter x 25.4 cm length). Details of the dialyzer are shown in Figure 3.

The dialysis unit was mounted on a 91.5 x 137.2 cm base which was movable with a forklift. The unit was equipped with two positive displacement gear pumps (maximum flow rate 18.9 L/min) driven by 3/4 horsepower variable speed electric motors. The feed pumps for wash water and stripping solution were connected to in-line filters (5 micron) followed by flow meters and were then connected to the appropriate inlet ports of the dialysis stack. Each feed line was fitted with a pressure gauge and a sample valve. The outlet ports on the dialysis stack were fitted with sample valves. The wash water outlet was equipped to send treated wash water to waste and the stripping solution outlet was equipped to recycle the stripping solution to the stripping solution feed tank. The assembled dialysis unit is shown in Figure 4.



NOTE: The assembly bolt holes in the end plates are not shown.

Figure 3. Details of dialysis stack components

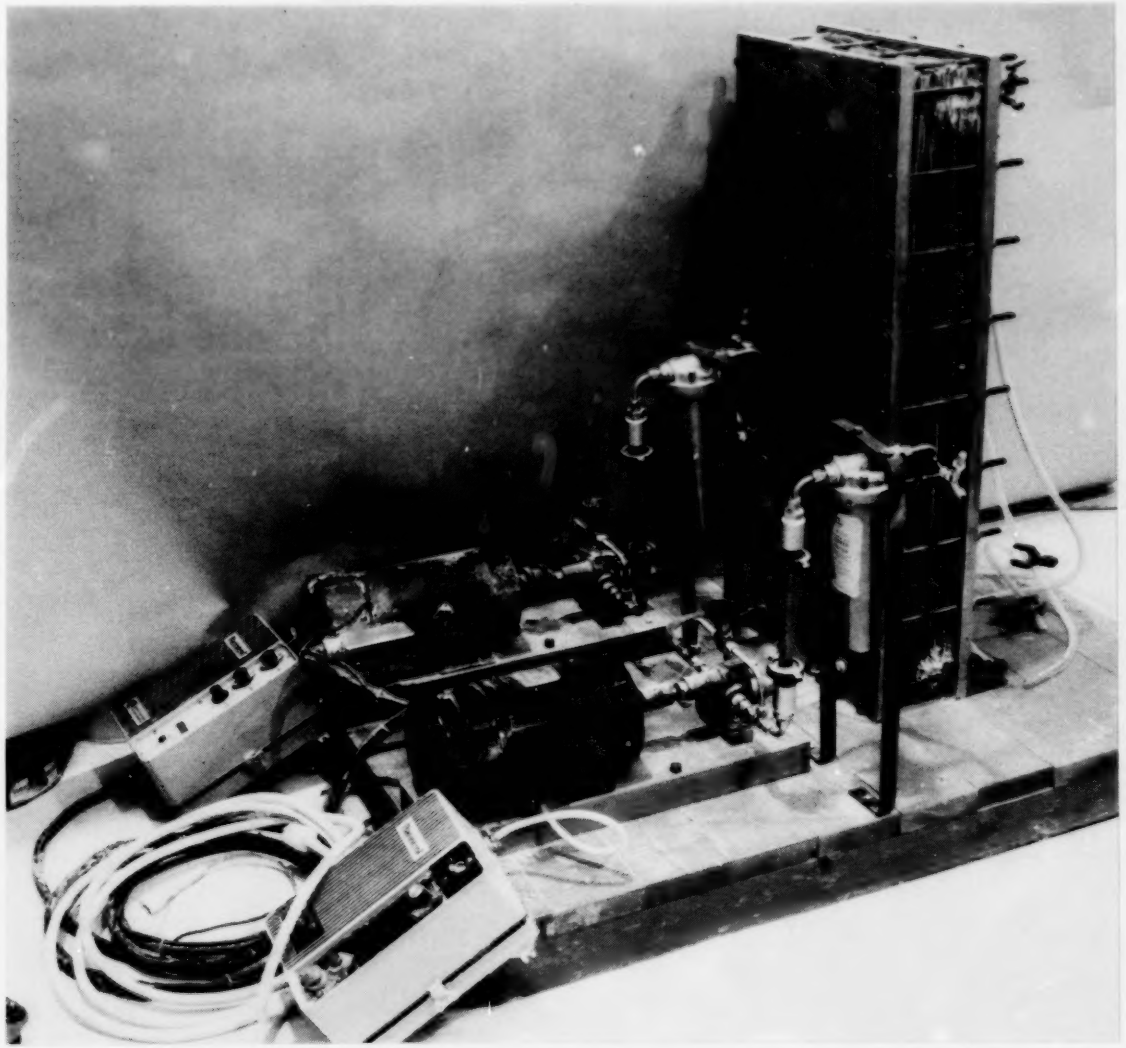


Figure 4. Prototype Donnan dialysis unit

SECTION 5

RESULTS AND DISCUSSION

THEORY OF DONNAN DIALYSIS

Ion-exchange resins are of utility in separation processes because they can be used to remove ions from dilute electrolyte solutions. When contacted with a stripping solution of the proper concentration, the resins release the ions. If ion-exchange resins are in membrane form, they can be in contact with the dilute electrolyte solution and the stripping solution simultaneously, and the ion-exchange process can be continuous rather than cyclic. This ion-exchange membrane process is based on the Donnan equilibrium principle (5) and requires no electrical current or high pressure for operations, as would be required for electrodialysis or reverse osmosis.

If solutions of two electrolytes are separated by an anion-exchange membrane, the cation composition of the two solutions must remain constant since the membrane is impermeable to cations. The anions, which can pass through the membrane, will redistribute between the two solutions until the Donnan equilibrium conditions are met. This equilibrium is defined by the following equation:

$$\left(\frac{(A^{-N})_l}{(A^{-N})_r}\right)^{\frac{1}{N}} = \left(\frac{(B^{-Z})_l}{(B^{-Z})_r}\right)^{\frac{1}{Z}} \qquad (1)$$

where A and B are mobile anions of valence -N and -Z, respectively, and l and r represent the solutions on the left and right sides of the barrier membrane.

For example, assume that the two solutions are 0.2M NaCl and 0.003M $Na_2[Cu(CN)_3]$. Due to the high concentration of Cl^- relative to the concentration of $[Cu(CN)_3]^=$, there will be an immediate flow of chloride ion across the membrane. Because the sodium ion cannot cross the membrane, there is a loss of electroneutrality in the solutions, and a charge potential builds across the membrane which is opposite in direction to the concentration potential gradient. This charge potential provides the driving force to transfer copper cyanide complex anions from the feed solution into the stripping solution. This process continues until the system comes to equilibrium.

Donnan (1) further showed that the driving force for redistribution of anions across a membrane was given by the expression.

$$DF = RT \ln \left\{ \left(\frac{A^-_r}{A^-_l} \right)^1 \cdot \left(\frac{B^{Z-}_l}{B^{Z-}_r} \right)^{\frac{1}{Z}} \right\} \qquad (2)$$

where DF is the driving force in joules/mole, R is the gas constant in joules/mole °K, T is the absolute temperature, A^- and B^{Z-} are the activities of the anions, and r and l refer to the solutions on opposite sides of the membrane.

The expression for the driving force for ion redistribution is derived from the expression for the Donnan potential, E_{Donnan}:

$$E_{Donnan} = \frac{RT}{Z_i F} \ln \frac{\bar{A}_i}{A_i} \qquad (3)$$

where R and T are as described above, Z is the valence of the i^{th} ionic species, F is the Faraday constant in coulombs, $\bar{A}_i$ is the activity of the anion in the membrane, and A_i is the activity of the anion in the external solution. The Donnan potential is the electric potential which exists at the solution-membrane interface and which provides the force for sorption of counterions (anions in this case) into the membrane and the exclusion of co-ions (cations in this case) from the membrane.

The Donnan potential can be seen to be concentration dependent. The activity of the sorbed anions within the membrane is determined by the concentration of fixed charged sites in the swollen polymer matrix and by the volume of water in the polymer matrix. This is a fixed quantity for a membrane and is controlled by ion-exchange capacity and equilibrium water content. The activity of the ions in dilute solution increases with increasing concentration. Increasing external ionic concentration decreases the Donnan potential since the term $\ln \bar{A}_i/A_i$ decreases as A_i increases and becomes zero when $A_i = \bar{A}_i$.

Donnan dialysis depends upon the permselectivity of the membrane. The maximum driving force for ion transport is realized when co-ions are perfectly excluded. When external ionic concentrations become too high, the Donnan potential decreases, co-ion exclusion diminishes, and co-ion leakage across the membrane occurs. The net result is lower driving force for ion transfer.

Donnan dialysis must be considered to be applicable to removal of ions from dilute solution. The specific concentration ranges for which selective ion transport can be obtained are determined by the ion-exchange capacity and equilibrium water content of each membrane.

EXPERIMENTAL RESULTS

The initial irradiation-initiated grafting run was made using the grafting solution compositions shown in Table 1. The irradiation was conducted at an applied dose rate of 12,000 rad/hour for 68 hours. Total applied dose was 0.85 mrad.

TABLE 1. GRAFTING SOLUTION COMPOSITION, FIRST EXPERIMENT

Film No.	Monomer	Wt % Monomer	Solvent
E-1	4-vinylpyridine	25	Methanol
E-2	4-vinylpyridine	25	Methanol
	N-vinyl-2-pyrrolidinone	15	
E-3	2-vinylpyridine	25	Methanol
E-4	2-vinylpyridine	25	Methanol
	N-vinyl-2-pyrrolidinone	15	
E-5	vinylbenzyl chloride	20	Benzene
E-6	vinylbenzyl chloride	40	Benzene
E-7	vinylbenzyl chloride	20	Benzene
	N-vinyl-2-pyrrolidinone	15	
E-8	vinylbenzyl chloride	40	Benzene
	N-vinyl-2-pyrrolidinone	15	

Dose rate: 12,000 rad/hr
Irradiation time: 68 hr
Total dose: 0.85 M rad

The membranes were characterized after quaternization. The properties of the membranes based on vinylbenzyl chloride grafting are given in Table 2.

TABLE 2. MEMBRANE PROPERTIES, FIRST EXPERIMENT

Membrane number	Quaternizing agent	Equilibrium water content g H_2O/g	Ion-exchange capacity meq/dry g
E-5-1	trimethylamine	0.904	1.34
E-6-1	"	0.971	2.47
E-7-1	"	0.843	1.28
E-8-1	"	1.823	2.70
E-5-2	tri-n-butylamine	0.678	0.74
E-6-2	"	0.982	0.75
E-7-2	"	0.918	0.22
E-8-2	"	1.260	0.51

The properties of the membranes quaternized with trimethylamine were good, but the ion-exchange capacities of the membranes quaternized with tri-n-butylamine were low. The quaternization reaction did not appear to proceed readily with the bulky tri-n-butylamine despite the 48-hour reaction period.

Attempts were made to determine complex metal ion transport rates for these membranes. No transport data could be obtained with any of the membranes due to membrane leaks.

The vinylpyridine-grafted films were placed in test cells and leak tested immediately after quaternization. Again, all membranes leaked. The vinylpyridine-based membranes were not characterized for equilibrium water content and ion-exchange capacity, since they were not usable for dialysis studies.

The film grafting procedures and the membrane quaternization procedures were reviewed in an attempt to ascertain the cause of the membrane leaks. As nearly as can be determined, the procedures did not deviate from the standard procedures which have been used for several years and which have consistently provided leak-free grafted membranes. Also, the base polyethylene film used was from an in-house supply which was prepared for SwRI by the film supplier as a single lot several years ago and which has consistently provided acceptable membranes in several prior studies.

A second grafting run to prepare eight grafted films for subsequent membrane preparation was made using the grafting solutions described in Table 3.

TABLE 3. GRAFTING SOLUTION COMPOSITION, FIRST EXPERIMENT

Film No.	Monomer	Wt % Monomer	Solvent
E-11	4-vinylpyridine	25	Methanol
E-12	4-vinylpyridine	25	Methanol
	N-vinyl-2-pyrrolidinone	15	
E-13	2-vinylpyridine	25	Methanol
E-14	2-vinylpyridine	25	Methanol
	N-vinyl-2-pyrrolidinone	15	
E-15	vinylbenzyl chloride	20	Benzene
E-16	vinylbenzyl chloride	40	Benzene
E-17	vinylbenzyl chloride	20	Benzene
	N-vinyl-2-pyrrolidinone	15	
E-18	vinylbenzyl chloride	40	Benzene
	N-vinyl-2-pyrrolidinone	15	

Dose rate: 12,000 rad/hr
Irradiation time: 68 hr
Total dose: 0.85 M rad

Precautions were taken to ensure that no deviations from standard grafting procedures occurred. A test fixture to leak test the films prior to and after quaternization was designed. Only membranes which passed the leak test were subjected to further characterization. Membranes from the second grafting experiment were of good quality; only an occasional specimen leaked, and the leaks could be identified as small tears or punctures introduced during membrane processing.

The grafted films were quaternized to provide strong base anion-exchange membranes. Portions of the vinylbenzyl chloride-grafted films were quaternized with trimethylamine (10% in H_2O) and with tri-n-butylamine (10% in methanol). Reaction time was 32 hours with trimethylamine and 90 hours with tri-n-butylamine. Portions of the vinylpyridine-grafted films were quaternized with methyl iodide (2% in methanol) and with 1-bromobutane (2% in methanol). Reaction time was 66 hours using methyl iodide and 114 hours using 1-bromobutane. The membranes were leak tested in the fixture previously described.

The quaternized membranes were characterized for equilibrium water content and ion-exchange capacity. The results are shown in Table 4.

TABLE 4. MEMBRANE PROPERTIES, SECOND EXPERIMENT

Membrane number	Quaternizing agent	Equilibrium water content g H_2O/g	Ion-exchange capacity meq/dry g
E11Q4	CH_3I	1.08	2.5
E11Q5	C_4H_9Br	1.09	0.9
E12Q4	CH_3I	2.45	2.6
E12Q5	CH_3I	1.86	1.1
E13Q4	CH_3I	1.02	0.6
E13Q5	C_4H_9Br	1.89	0.6
E14Q4	CH_3I	0.90	0.7
E14Q5	C_4H_9Br	0.80	0.2
E15Q1	$(CH_3)_3N$	0.83	1.1
E15Q2	$(CH_4H_9)_3N$	0.75	0.4
E16Q1	$(CH_3)_3N$	1.52	2.2
E16Q2	$(C_4H_9)_3N$	0.87	1.2
E17Q1	$(CH_3)_3N$	0.62	1.0
E17Q2	$(C_4H_9)_3N$	0.73	0.5
E18Q1	$(CH_3)_3N$	1.00	2.2
E18Q2	$(C_4H_9)_3N$	1.35	1.4

Quaternization Reaction Conditions:

CH_3I (2% in methanol) for 66 hours
C_4H_9Br (2% in methanol) for 114 hours
$(CH_3)_3N$ (10% in water) for 32 hours
$(C_4H_9)_3N$ (10% in methanol) for 90 hours

Several membranes were evaluated for metal ion transport. Results are shown in Table 5.

TABLE 5. MEMBRANE TRANSPORT DATA

Membrane number	Ion-exchange capacity meq/dry g	Osmotic water flow rate mL/hr/cm^2*	Metal complex anion transport rate constant** min^{-1}		
			Cu	Cd	Zn
E11Q4	2.5	0.040	3.1	2.8	1.9
E12Q4	2.6	0.053	2.3	2.2	2.9
E12Q5	1.1	0.010	0	–	–
E14Q4	0.7	0.010	1.1 (1.1)†	0.3	0.2
E15Q1	1.1	0.012	1.0	0.4	0.1
E16Q1	2.2	0.102	2.5	–	–
E16Q2	1.2	0.016	0	–	–
E18Q1	2.2	0.054	2.2	1.4	0.6
E18Q2	1.4	0.009	0	–	–

* 0.2N NaCl versus deionized H_2O--cell effective area 122 cm^2.
** Feed-nominal 50 ppm in metal of interest; stripping solution 0.2N NaCl.
† Duplicate determinations of the rate constant.

All membranes that showed transport were evaluated for copper, cadmium and zinc as their cyanide complex anions. Membranes that displayed a zero transport for copper (E12Q5, E16Q2 and E18Q2) were not further evaluated. It can be seen that these three films were prepared using more bulky quaternizing reagents (1-bromobutane for E12Q5 and tri-n-butylamine for E16Q2 and E18Q2). The comparable membranes quaternized with less bulky quaternizing reagents (methyl iodide for E12Q4 and trimethylamine for E16Q1 and E18Q1) displayed normal transport of the metal complex anions. Since the ion-exchange capacities and equilibrium water concentrations of all the membranes are roughly comparable, it would appear that the increased steric requirements of the more bulky quaternizing groups preclude ion transport. However, this rationale is speculative due to the limited data available.

The trend that is readily apparent in the data in Table 5 is a positive correlation of metal ion transport rate with ion-exchange capacity. Increased ion-exchange capacity appears to lead to increased metal ion transport rates. Additionally, it was determined that there was a positive correlation between osmotic water flow rate and ion-exchange capacity.

The rate constants for metal transport decrease in the order of copper > cadmium > zinc in all cases except one, in which the above order is reversed. The value for copper in this reversed sequence at 2.3 is larger than the value for cadmium at 2.2. However, within the precision of the data these two numbers are probably not different. The order of decrease corresponds to the order in which the rate constants were determined. The procedure usually followed in the laboratory involved the determination of the copper

transport rate constant, rinsing out the test system with deionized water, the determination of the cadmium transport rate constant, rinsing out the system with deionized water, and the determination of the zinc transport rate constant. Since the only case where the sequence of the determinations was reversed led to a reversal of the order of decrease in the rate constants, it was considered that the decreases in the rate constants might be a result of changes in the membrane from run to run.

Therefore, a series of determinations of metal ion transport rate constants for Membrane E14Q4 was made. The results are presented in Table 6. Initially, duplicate determinations of the copper transport rate constant were made and were found to be the same (1.1, 1.1) within the precision of the experimental data. Next the system was rinsed with deionized water, the cadmium transport rate constant (0.3) was determined, the system was water rinsed, the zinc transport rate constant (0.2) was determined, the system was water rinsed, and the copper transport rate constant (1.0) was again determined. This latter value does not appear to be significantly different from the initial duplicate determinations for copper.

TABLE 6. EFFECT OF MEMBRANE* TREATMENT ON METAL ION TRANSPORT

Treatment	Metal ion transport rate after treatment, min^{-1}		
	Cu	Cd	Zn
Deionized water rinse	1.1 (1.1)** (1.0)†	0.3	0.2
1.8% HCl rinse	1.5 1.6	0.5	0.3
Repeat deionized water rinse	–	0.5	0.3

* Membrane E14Q4
** Duplicate determination
† Repeat determination made after the cadmium and zinc determinations

The test system was then rinsed by recirculation of 4 liters of 1.8% hydrochloric acid. The copper transport rate constant was redetermined to be 1.5 min^{-1}, a significant increase. Cadmium and zinc transport rate constants were also redetermined, with intermediate 1.8% hydrochloric acid rinses, and were found to be 0.5 min^{-1} and 0.3 min^{-1}, respectively. Both of these increases appear to be significant. Finally, the series of rate constants was determined again. The system was rinsed with 1.8% hydrochloric acid and rinsed with deionized water, and the copper transport rate constant was determined to be 1.6 min^{-1}. Cadmium and zinc transport rate constants were determined with only intermediate deionized water washes. Their rate constants were 0.5 min^{-1} and 0.3 min^{-1}, respectively.

As can be seen, the initial acid treatment lead to a significant increase in metal ion transport rate constant for all three metals, the subsequent acid treatment having no effect. Finally, the membranes in the system were leak tested and found to be leak free.

Inasmuch as the acid treatment of Membrane E14Q4 lead to increases in the metal ion transport rates from 45 to 67%, it was decided to try this treatment on more promising membranes.

As was stated earlier, it was found that the rate of metal ion transport increased with increasing ion-exchange capacity. Four candidate membranes, whose properties are shown in Table 7 along with those of E14Q4, were chosen for acid treatment. The ion-exchange capacities of these membranes range from 2.2 to 2.6 meq/dry gram, compared to a value of 0.7 meq/dry gram for E14Q4.

TABLE 7. MEMBRANE PROPERTIES, ACID TREATMENT STUDY

Membrane number	Membrane type	Equilibrium water content g H_2O/g	Ion-exchange capacity meq/dry g
E11Q4	(4-VP)CH_3I	1.08	2.5
E12Q4	(2-VP/N-VP)CH_3I	2.45	2.6
E14Q4	(4-VP/N-VP)CH_3I	0.90	0.7
E16Q1	(VBC)$(CH_3)_3N$	1.52	2.2
E18Q1	(VBC/N-VP)$(CH_3)_3N$	1.00	2.2

4-VP - 4-vinylpyridine
2-VP - 2-vinylpyridine
N-VP - N-vinyl-2-pyrrolidinone
VBC - vinylbenzyl chloride

The procedure for testing these membranes involved leak testing, determination of osmotic water transport rate, determination of the copper transport rate constant, acid treatment with 1.8% hydrochloric acid, determination of the copper transport rate constant, determination of the osmotic water transport rate (with one exception), and a final leak check.

As can be seen from the data in Table 8, two of the candidate membranes (E11Q4 and E12Q4) showed a decrease in the rate constant, one (E16Q1) showed a modest increase in the rate constant, and one (E18Q1) showed essentially no change. The osmotic water flow rates remained essentially unchanged except E12Q4 which increased. However, the significant finding was that all four candidate membranes leaked after the acid treatment.

TABLE 8. MEMBRANE TRANSPORT DATA, ACID TREATMENT STUDY

Membrane number	Osmotic water flow rate, mL/hr/cm^2		Copper transport rate constant, min^{-1}		Comments
	Initial	After acid treatment*	Original	After acid treatment	
E14Q4	0.006	0.007	1.1(1.1)**	1.5(1.6)**	Membrane passed post-acid treatment leak test.
E12Q4	0.048	0.083	3.2	2.1	Membrane failed post-acid treatment leak test.
E11Q4	0.056	-	3.1	2.1	,,
E16Q1	0.102	0.113	2.5	2.8	,,
E18Q1	0.090	0.094	2.6	2.5	,,

* Membranes treated for 1 hour at ambient temperatures with 1.8% hydrochloric acid.

** Duplicate determinations.

The mechanism by which the acid treatment might lead to enhanced metal transport rates is not known, but it appears to affect the membrane structure in such a way so as to weaken the high ion-exchange capacity membranes and lead to leaks. Therefore, the acid treatment does not appear to be a viable procedure for use with high ion-exchange capacity membranes. Additionally, it does not sufficiently enhance the metal transport rate for a low ion-exchange capacity membrane to give membranes comparable to untreated high ion-exchange capacity membranes.

The four membranes that showed the highest metal ion transport rate constants when operating with low levels of metal ion (about 50 ppm) in the feed were selected for further evaluation with higher concentrations of metal ion in the feed. These four membranes, whose properties are shown in Table 9, all have ion-exchange capacities in excess of 2 milliequivalents per gram. Two membranes are based on vinylpyridine-grafted polyethylene, and two are based on vinylbenzyl chloride-grafted polyethylene film.

TABLE 9. PROPERTIES OF HIGH TRANSPORT RATE MEMBRANES

Membrane number	Membrane type	Equilibrium water content g H_2O/g	Ion-exchange capacity meq/dry g	Osmotic water flow rate* mL/hr/cm^2
E11Q4	(4-VP)CH_3I	1.08	2.5	0.040
E12Q4	(4-VP/N-VP)CH_3I	2.45	2.6	0.048
E16Q1	(VCB)$(CH_3)_3N$	1.52	2.2	0.102
E18Q1	(VBC/N-VP)$(CH_3)_3N$	1.00	2.2	0.090

*0.2N NaCl versus deionized H_2O--cell effective area 122 cm^2.

The dialysis runs were made using the normal procedure except that the metal ion content of the feed was nominally 500 ppm and the concentration of the stripping solution was 1 normal sodium chloride. The low level runs had been made with nominal 50 ppm feed and 0.2 normal sodium chloride. Therefore, it can be seen that the ratio of stripping solution concentration to feed concentration with the high level feed is only one half of that ratio for the low level feed. The end result is that the driving force for metal ion transfer is lower for the high level feed than for the low level feed.

It was necessary to use the lower stripping concentration/feed concentration ratio to ensure that the membranes maintained their ion selectivity as previously discussed under Theory of Donnan Dialysis in Section 5 of this report.

The results obtained with the four membranes are presented in Table 10. All four membranes showed good transport rate constants with the low level feed solutions. However, Membranes E12Q4 and E16Q1 showed significantly lower rate constants with the high level feeds. Membrane E11Q4 showed decreased rate constants with the high level feed, but the rate constants still are acceptably high. The performance of Membrane E18Q1 was better than E12Q4 and E16Q1 but inferior to that of E11Q4. The reduction in rate constants is certainly due in part to the decreased driving force for ion transport described above. However, the significantly larger decreases observed for Membranes E12Q4 and E16Q1 as compared to E11Q4 and E18Q1 are most probably due to the higher hydrophilicity of the former two membranes, as indicated by their higher equilibrium water contents shown in Table 9. This higher water content leads to a larger swollen volume and a reduced ionic concentration in these membranes. Therefore, these two membranes would be expected to develop a lower Donnan potential than that developed by the two less hydrophilic membranes. The reduced Donnan potential leads to less ion selectivity; cation leakage across the membrane occurs, and the driving force for anion transfer from the feed to the stripping solution is decreased.

TABLE 10. EFFECT OF METAL ION CONCENTRATION ON ION TRANSPORT

Membrane	Metal ion transport rate, min^{-1}					
	Low concentration*			High concentration**		
	Cu	Cd	Zn	Cu	Cd	Zn
E11Q4	3.1	2.8	1.9	1.5	1.5	1.5
E12Q4	2.3	2.2	2.9	0.7	0.8	0.6
E16Q1	2.5	1.6	0.7	0.6	0.9	- †
E18Q1	2.2	1.4	0.6	1.41	0.6	0.4

* Nominal 50 ppm in metal ion.
** Nominal 500 ppm in metal ion.
† Membrane ruptured.

Membrane E11Q4, based upon 4-vinylpyridine, gives the most consistent performance as can be seen in Table 10. Two additional portions of the 4-vinylpyridine-grafted films were quaternized with methyl iodide in separate reactions. After quaternization, sections of these membranes, designated E11Q4-B and E11Q4-C, were leak tested. After being shown to be leak-free, they were evaluated in the membrane test system using all three metal ions at both low and high metal ion concentrations. The results obtained with these two membranes are shown in Table 11 along with the previously reported transport rate constants for Membrane E11Q4 (Table 10).

TABLE 11. REPLICATE EVALUATIONS OF MEMBRANE E11Q4

	Metal ion transport rate, min^{-1}					
	Low concentration*			High concentration**		
Membrane†	Cu	Cd	Zn	Cu	Cd	Zn
E11Q4‡	3.1	2.8	1.9	1.5	1.5	1.5
E11Q4-B	3.4	3.1	2.0	1.5	1.3	1.3
E11Q4-C	3.2	2.7	2.1	1.6	1.4	1.3

* Nominal 50 ppm in metal ion
** Nominal 500 ppm in metal ion
† Separate sets of membranes--same grafting run, separate quaternization reaction
‡ From Table 10

The data indicate reasonably consistent performance by the three sets of membranes. The observed differences may be due to lack of total uniformity along the 7.62-m length of grafted film. However, it is felt that the observed differences in the metal ion transport rate constant are not practically significant with regard to use of such membranes in a Donnan dialyzer for simulated rinse water treatment.

The initial task on the second program was the synthesis of sufficient membrane to assemble the prototype dialyzer. These membranes were to duplicate the properties of Membrane E11Q4. The target specifications were equilibrium water content of about 1 g H_2O/g membrane, ion-exchange capacity of about 2.5 meq/dry g, osmotic water flow rate of about 0.04 mL/hr cm^2, and a metal ion transport rate constant of about 1.5 min^{-1} for Cu, Cd and Zn as their complex cyanide anions at a concentration of 500 ppm in the feed rinse water using 1.0N NaCl as the stripping solution.

The initial membrane synthesis utilized 11 rolls (36.6 cm x 30.5 m) of film. The film was grafted with 4-vinylpyridine and quaternized with methyl iodide as described above.

The membranes (five rolls out of eleven total) were characterized for equilibrium water content, ion-exchange capacity, osmotic water flow rate, and metal ion transport rate. The results obtained are given in Table 12, except for the metal ion transport rate constants.

TABLE 12. MEMBRANE PROPERTIES OF INITIAL GRAFTING RUN

Roll no.	Equilibrium H_2O content, g/dry g*	IEC meq/dry g	Osmotic water flow rate mL/hr/cm^2
1	0.682 ± 0.072	1.78	0.041
3	0.581 ± 0.063	1.97	0.036
7	0.571 ± 0.074	1.94	0.040
8	0.721 ± 0.112	2.07	0.044
11	0.731 ± 0.141	2.01	0.048

* Mean and standard deviation; three determinations

Triplicate determinations of equilibrium water content were made. There was considerable variation in the individual determinations for the three samples from each membrane with percent relative standard deviations ranging from 10.5 to 19.3%. The ion-exchange capacities were consistent around the value of 2.0 meq/g except for Membrane 1, which was low at 1.78. Osmotic water flow rates were consistent at about 0.04 mL/hr/cm^2 when determined using deionized water on one side of the membrane and 1.0N NaCl on the other side.

Problems arose when determination of metal ion transport rates was initiated using the laboratory Donnan dialysis test system. Membrane 11, which was initially evaluated, gave a copper transport rate constant of 1.52 min^{-1}, cadmium transport rate constant of 1.41 min^{-1}, and zinc transport rate constant of 1.38 min^{-1}. Evaluation of Membrane 8 gave a copper transport rate constant of only 0.66 min^{-1}, even though the ion-exchange capacity and equilibrium water content of this membrane are very close to the values obtained from Membrane 11. Samples of Membranes 3 and 7 were evaluated for copper transport and were found to have rate constants of 1.12 min^{-1} and 0.43 min^{-1}, respectively. At this time, samples of the membranes listed in Table 12 were taken at several places along the 30.5-m length of each membrane. Infrared spectra of the membrane samples were taken and compared. It was found that the membranes were not of uniform composition along their lengths. This nonuniform grafting of the 4-vinylpyridine along the length of the polyethylene was most probably due to variation in tension on the polyethylene film and cheesecloth backing rolls when the film-cheesecloth backing was being rolled onto rods in preparation for the grafting reaction. Excess tension in the rolling process results in the film-cheesecloth being wound too tightly. As a result, diffusion of the 4-vinylpyridine grafting solution into the roll during grafting is restricted, and a low degree of grafting is obtained in those areas.

A second grafting run, utilizing six film rolls in a single reactor was conducted. Care was taken to ensure that the film-cheesecloth rolls were loosely wound. After grafting and washing, samples were taken at intervals along the length of the films. Infrared spectra indicated that the films were uniformly grafted. These films were quaternized with methyl iodide and samples were taken for metal ion transport rate determinations.

It was found that the metal ion transport rate constant decreased with time. Initial values of 1.4-1.6 min^{-1} were obtained, but these values declined to less than 0.5 min^{-1} in several hours of dialyzer operation.

Infrared spectra of the unused samples of the membranes showed very strong absorption bands for the quaternized polyvinylpyridine.

Samples of the quaternized membrane were washed with 10% hydrochloric acid and with 10% sodium hydroxide. Acid washing produced no change in the infrared spectra, but caustic washing led to loss of most of the absorption band intensity for quaternized polyvinylpyridine. The application of caustic washing to the membranes from the initial grafting experiment gave identical results.

It was concluded that the films had not grafted appreciably. The strong infrared absorption bands were attributed to occluded polyvinylpyridine homopolymer within the film. After quaternization, the resulting water-soluble polyvinyl-N-methylpyridinium iodide leached out of the film.

SwRI TECHNICAL REVIEW

Inasmuch as good membranes were prepared on the initial study by grafting 4-vinylpyridine onto polyethylene followed by quaternization with methyl iodide using the above procedures, a review of possible differences in this work and the previous work was undertaken. The results of this review follow.

1) Polyethylene Film--The film used in the previous and present studies was from a special lot purchased several years ago.

2) Cheesecloth Interleaving--The cheesecloth used in the present and previous studies was from a lot purchased several years ago.

3) Solvent--ACS grade methanol was used as the grafting solvent. GC/MS analysis of the methanol did not reveal any significant impurities which might affect the grafting reaction.

4) Monomer--The work on the previous project was conducted using 4-vinylpyridine purchased from Aldrich Chemical Company. The 4-vinylpyridine used in the present work was purchased from Riley Tar and Chemical Company, the major producer of this chemical in the United States. The monomer was purchased from Riley due to the large volume required. Monomers from both suppliers were subjected to GC/MS analysis. There was no significant difference in the monomers; both were 99.8% plus 4-vinylpyridine. The trace impurities in both monomers (mostly alkylpyridines) should not affect the grafting reaction.

5) Radiation Dose Rate--For a number of years, all dosimetry at SwRI was performed using the Bausch and Lomb cobalt glass chip system. In this system, a special cobalt glass chip is irradiated and the change in optical density at a specified wavelength is

determined using a spectrophotometer. The total radiation dose is read from a calibration curve which gives change in optical density as a function of dose. Dividing the total dose by the irradiation time gives the dose rate. The cobalt glass was quite sensitive to dose and was good for determining low dose rates. Bausch and Lomb has discontinued production of this dosimeter material. SwRI currently uses lithium fluoride crystal dosimeters. These are used in the same manner as the cobalt glass. However, the lithium fluoride is much less sensitive, and the precision of determination of low dose rates is poor unless very long irradiation times are employed to provide a large total dose. It is possible that the irradiation dose rate was lower than desired in the irradiations. However, a check of the two dosimetry systems against each other, using the few cobalt glass chips available, gave comparable dose rate measurements.

In an attempt to resolve the problems encountered, three film grafting experiments were conducted using the standard grafting procedure. Single 7.62-m film rolls were used. In one experiment, grafting solutions were prepared using 4-vinylpyridine from Aldrich Chemical Company and Riley Tar and Chemical. These films were irradiated at 12,500 rad/hour for 68 hours. The films were washed and quaternized as described above. Both films showed the same instability in base as described above.

A second experiment was conducted in which 7.62-m rolls of film were grafted using 4-vinylpyridine and 2-vinylpyridine (Aldrich Chemical Company). The irradiation was conducted at 43,000 rad/hour for 68 hours. After workup and quaternization, the 4-vinylpyridine-grafted film was unstable in basic media. However, the 2-vinylpyridine-grafted film, after washing and quaternization, was stable. The possibility exists that the membrane prepared on the previous project was grafted with 2-vinylpyridine rather than 4-vinylpyridine if a mistake was made in charging the grafting solutions into the reaction vessel. The metal ion transport rate constant for the 2-vinylpyridine film was found to be 0.4 min^{-1} which is typical of the rates previously seen with 2-vinylpyridine membranes.

The third run incorporated small amounts (1, 2 and 4 volume %) of divinylbenzene (DVB) in the grafting solution along with 4-vinylpyridine (25%) and methanol (71 to 74%). This experiment was conducted based on a report in the literature that inclusion of small amounts of divinylbenzene in the grafting solution enhances the radiation grafting of polymers with monofunctional monomers (6). One 7.62-m roll was grafted with 25% 4-vinylpyridine in methanol to serve as a control. Since the addition of divinylbenzene leads to cross-linking of the grafted film, the hydrophilicity is reduced which reduces the metal ion transport rate. One film was grafted using 4-vinylpyridine (25%), divinylpyridine (4%), and N-vinyl-2-pyrollidinone (5%). The N-vinyl-2-pyrollidinone was added to increase the hydrophilicity of the grafted film.

After washing and quaternization, the film grafted with 4-vinylpyridine only was unstable in base. The four films grafted with DVB-containing grafting solution were all stable in base. The film grafted with DVB and

N-vinyl-2-pyrrolidinone gave a very low metal ion transport rate constant ($0.11\ min^{-1}$). The film prepared using 1% DVB had a rate constant of 0.61; the film prepared using 2% DVB had a rate constant of 0.86; and the film prepared using 4% DVB had a rate constant of $0.08\ min^{-1}$ when dialyzing approximately 500 ppm Cu against 1N sodium chloride stripping solution.

The addition of a difunctional monomer (DVB) to the grafting solution gave 4-vinylpyridine-grafted membranes which were stable to base. However, these membranes all had rate constants which were appreciably lower than the value ($1.5\ min^{-1}$) obtained with Membrane E11Q4.

In view of the fact that inclusion of small amounts of divinylbenzene incorporated into the grafting solution led to base-stable 4-vinylpyridine-grafted membranes, an experiment was conducted to further explore the possibility of a similar synergistic effect with other monomers in admixture with 4-vinylpyridine. The monomers chosen included 2-vinylpyridine, N-vinyl-2-pyrrolidinone, and vinylbenzyl chloride. These three monomers were in use in the first membrane development program, and the possibility existed for inadvertent contamination of the 4-vinylpyridine grafting solution used to prepare E11Q4 with one of the monomers. Grafting solutions containing 1 wt % of each of these monomers along with 4-vinylpyridine were prepared. Standard grafting procedures were followed. All grafted films were found to be unstable to base after quaternization. Also included in this grafting experiment was evaluation of the use of a chain transfer agent (5 wt % carbon tetrachloride) and the use of water-methanol (1:6.5) solvent. The aqueous methanol was used since in some graft polymerizations in which a water-sensitive copolymer is produced, water has an accelerating effect on the grafting reaction. Neither of these two variations produced a base-stable membrane.

One final experiment was conducted to determine the effect of the crystallinity of the base polyethylene on the stability of the grafted film. The infrared spectrum of polyethylene displays a doublet at 720 and 730 cm^{-1} which is related to the relative crystallinity of the resin. These two absorptions are due to methylene rocking frequencies in the polymer backbone chain. The variation in frequency is caused by the different energies required by the differences in chain stiffness and interchain distances in the crystalline and amorphous regions. The relative intensities of these two bands cannot be used to quantitatively determine the crystalline content of the resin; however, comparison of the spectra of a series of samples will show differences in the crystalline/amorphous ratios in the samples. Inspection of the spectra of E11Q4 and several other 4-vinylpyridine-grafted films showed differences in the relative intensities of these two bands.

A series of spectra were taken on samples of film from the supply used in this work. This film was prepared from Dow 400 polyethylene resin and was from a single lot. However, the film has been on hand for about 12 years, and the various rolls have been stored under varying conditions: in the laboratory under air conditioning, in the stockroom with less control of ambient temperatures, and in a warehouse with no control of ambient conditions. Also, two other rolls of film prepared from Dow 110E and Dow

510E resins were available. Varying ratios of the two absorption bands were observed for the different rolls of Dow 400 film and for the rolls of Dow 110E and 510E films. It was also found that annealing a Dow 400 film overnight at 108°C followed by rapid cooling in air led to a reversal in the absorption intensities of the two peaks, compared to the unannealed sample. A grafting experiment was conducted in which several samples of Dow 400 film, one of Dow 110E film and one of Dow 510E film were grafted with 4-vinylpyridine. Included were two samples of annealed Dow 400 film, one cooled slowly and one cooled rapidly after annealing. After processing and quaternization, all films were found to be unstable in base. The primary difference in these grafted films was the degree of grafting which ranged from 47.7% to 66.3%. The two films with the lowest degree of grafting were the annealed films. The rapidly cooled film showed a degree of grafting of 56.8%, and the slowly cooled film showed a degree of grafting of 47.7%.

EXTERNAL TECHNICAL REVIEW

At this point, arrangements were made for outside peer review to assess the status of the program and to make recommendations for further work. The peer review group included two representatives of the U.S. Environmental Protection Agency, a representative of the American Electroplaters Society, and two industry consultants. The two industry consultants were recognized authorities in the area of membrane separation processes and both have been active in research relating to Donnan dialysis for a number of years. Two representatives of Southwest Research Institute attended.

This group reviewed the technical efforts described above. It was concluded that the reasons for the instability of all 4-vinylpyridine-grafted membranes prepared subsequent to the synthesis of Membrane E11Q4 were not known. The peer reviewers also concluded that while the above-described attempts at resolving the problem were reasonable and diligently pursued, further efforts at resolving the problem were not justified at the present time. It was recommended that no further work on the problem of membrane instability be undertaken. It was further recommended that the best available, stable SwRI membranes be compared with representative commercially available membranes. The best membrane available, either SwRI produced or commercially available, should be selected. The prototype should be fabricated using this membrane, and the field evaluation conducted. Three commercially available membranes were obtained from the manufacturer. These membranes, along with several SwRI membranes, were evaluated in the laboratory dialysis system.

The three commercial membranes were described by the vendor as follows: C-1 and C-2 are based upon vinylbenzyl chloride-grafted films which were quaternized with trimethylamine after grafting, while C-3 was a vinylpyridine-grafted polyethylene membrane. This latter membrane was soaked in dilute base for 24 hours, rinsed with deionized water until the rinse water was neutral, and dried at 50°C for 24 hours to quaternization with methyl iodide, following instruments issued by the vendor.

Four SwRI membranes were also evaluated. Membrane SW-3-2 was polyethylene grafted with 2-vinylpyridine and quaternized with methyl iodide. Membrane

SW-3-4 was polyethylene grafted with vinylbenzyl chloride and quaternized with trimethylamine. The other two SwRI membranes tested were grafted using mixtures of 4-vinylpyridine/styrene in the grafting solution. These membranes were prepared on an internal study, one aspect of which involved synergistic effects of one monomer with another during grafting. The weight ratio of 4-vinylpyridine to styrene in SW-3-3 was 13.5:1 and the ratio in SW-3-6 was 2.7:1. After quaternization of these films with methyl iodide, they were found to be stable under the basic conditions experienced in the dialysis system; therefore, they were included in the evaluation. The remaining two SwRI membranes (SW-R-3 and SW-R-5) are from the batch prepared for the prototype dialyzer and will be discussed later.

The results of the film evaluation are given in Table 13.

TABLE 13. MEMBRANE EVALUATION

Membrane number	Source	Type	Osmotic water transport* mL/hr/cm^2	Copper removal rate constant** min^{-1}
C-1	Commercial	VBC	0.026	0.20
C-2	Commercial	VBC	0.017	0.31
C-3	Commercial	4-VP	-†	-†
SW-3-3	SwRI	4-VP/ST	0.071	0.61
SW-3-6	SwRI	4-VP/ST	0.068	0.28
SW-3-2	SwRI	2-VP	0.052	0.30
SW-3-4	SwRI	VBC	0.054	0.18
SW-R-3	SwRI	4-VP/ST	0.059	0.75
SW-R-5	SwRI	4-VP/ST	0.061	0.77

* Deionized H_2O versus 1.0N NaCl
** 500 ppm Cu feed; 1.0N NaCl strip
† Not determined--membrane unstable

VBC vinylbenzyl chloride
4-VP 4-vinylpyridine
2-VP 2-vinylpyridine
ST styrene

The membranes were evaluated for osmotic water transport using deionized water on one side of the membrane and 1.0N sodium chloride on the other. They were also evaluated for metal ion transport by determining the first order rate constant for complex copper cyanide anion using a feed that was 500 ppm in copper and 1.0N sodium chloride stripping solution.

The two commercial membranes based on vinylbenzyl chloride (C-1 and C-2) both had low osmotic water transport rates. The copper transport rate constants were 0.20 and 0.31 min^{-1}, respectively.

The vinylbenzyl chloride-based SwRI Membrane SW-3-4 had an osmotic water transport rate 0.52 mL/hr/cm^2, approximately twice that of the corresponding commercial membranes, while the copper transport rate constant was comparable at 0.18 min^{-1}. The SwRI membrane based on 2-vinylpyridine was also comparable with a copper transport rate constant of 0.30 min^{-1}.

The commercial vinylpyridine membrane (C-3) was not evaluated in the dialysis system. This membrane, after quaternization with methyl iodide, showed the same instability in basic solution observed with 4-vinylpyridine-based membrane prepared at SwRI. Upon being placed in basic solution, the membranes immediately turned brown followed by a slower change to dark green. The solution also assumed a green color. After 1 to 2 hours exposure to base, the membrane was washed with dilute hydrochloric acid, washed neutral, and air dried. Comparison of infrared spectra of the base treated film and the freshly quaternized film indicated that the major portion of the polyvinylpyridine in the grafted film was removed by base treatment.

MEMBRANE SELECTION AND DIALYZER TESTING

As mentioned above, two membranes prepared with mixtures of styrene and 4-vinylpyridine in the grafting solution were found to be base-stable after quaternization. These two films (SW-3-3 and SW-3-6) had comparable osmotic water transport rates. However, the copper transport rate constants were significantly different. Membrane SW-3-6, which contained the larger amount of styrene, had a rate constant of 0.28 min^{-1}, comparable to the other membranes in the table. The low styrene content film, SW-3-3, had a rate constant of 0.61 min^{-1}, approximately twice that of the other membranes. This membrane was chosen for use in the prototype dialyzer.

Six 36.6 cm x 30.5 m rolls of polyethylene were grafted in a single reactor using a grafting solution consisting of 4-vinylpyridine (24.4 wt %), styrene (3.6 wt %) and methanol (72.0 wt %). Irradiation was at 12,500 rad/hr for 68 hours. The grafted film was washed free of homopolymer and quaternized. Samples (SW-R-3 and SW-R-5) from two rolls, chosen at random, were evaluated in the laboratory dialyzer. Osmotic water transport rates were slightly lower than for SW-3-3, and the copper transport rate constants were about 25% greater. These membranes were selected for incorporation into the prototype dialyzer. The membranes were cut to size and leak tested. Assembly of the dialyzer stack was completed, and the dialysis unit was assembled. The dialysis unit consisted of two pumps, one for feed and one for stripping solution. Each pump was equipped with a particulate filter, a flow meter (0 to 10 gpm) and a pressure gauge. Sample valves at the dialyzer stack inlet and outlet were provided for both the feed stream and the stripping solution stream, as previously described.

After assembly the unit was checked for operability by pumping water through both the feed and stripping solution pumps. System backpressures were 10 to 15 psi at 2 to 4 gpm flow rates. After a short period of operation, leaks developed in the dialyzer stack. The stack was disassembled and examined. It was found that the leaks developed in the flow spacer gaskets. These gaskets are a laminated structure consisting of neoprene rubber-silicone rubber-neoprene rubber, the silicone rubber serving to impregnant and seal the periphery of the polypropylene mesh flow spacers. The neoprene rubber-silicone rubber interfaces had delaminated in some areas which led to leaks.

The flow spacers were reassembled using a liquid rubber adhesive. Additionally, as each flow spacer-membrane assembly was placed in the dialysis stack the adhesive was used to ensure good spacer-to-spacer bonding. The

bolts which secured the aluminum end plates of the stack were torqued to 70 lb-ft.

The reassembled dialysis stack was subjected to flow testing at 1.0 to 1.2 gpm flow rate through both the feed and stripping solution pumps. There were no initial problems; however, after approximately 33 hours of operation (5 to 6 hours per day), it was noticed that the volume of water in the strip tank was increasing and the volume of water in the feed tank was decreasing, indicating internal leaks. The pressure drop across the dialysis stack was 35 to 40 psi at flow rates of 1.0 to 1.2 gpm. It was not possible to control the feed and strip pressure at identical values with the manually controlled feed pump. A pressure differential between the feed and strip of about 3 to 5 psi was normally seen, and the leaks were from the high pressure stream to the low pressure stream.

It was not determined whether the leaks were due to defects in the spacer assemblies or due to physical defects developing in the membranes. Since the spacer-membrane assemblies were bonded together during reassembly of the dialysis unit, an attempt to disassemble the unit would probably result in a certain amount of physical damage to the components and would obscure the cause of the leaks; however, it does appear that the present design is not viable for a dialysis unit with the dimensions employed.

Review of the project led to the conclusion that a major redesign of the dialysis unit would be required. After consideration of both the financial and time factors involved in such a redesign effort, it was decided to terminate the project.

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APPENDIX A

SAMPLING AND ANALYTICAL PLAN

SUMMARY

The objective of the program was the synthesis and characterization of anion selective ion-exchange membranes for use in removal of toxic metals from wash waters by Donnan dialysis. The metals of interest were zinc, copper and cadmium (as their complex cyanide anions) in electroplating wash waters. The membranes were evaluated by determining the rate constant for transport of the complex metal ions across the membrane. Feed solutions containing the metal ion were fed to one side of the dialysis cells, and a strip solution was fed to the other side of the cells. Determination of the rate constants required knowledge of the metal ion concentration in the inlet to and outlet from the dialysis cell at steady-state conditions.

PURPOSE OF SAMPLING AND ANALYSIS

The sampling and analyses were conducted for the purpose of providing data which allowed the determination of the rate constants for metal removal from the wash water. The rate constants were calculated using the equation:

$$k = \frac{\ln \frac{C_o}{C}}{t}$$

where k - metal removal rate constant
C_o - concentration of the metal ion in the feed to the dialysis cell
C - concentration of the metal ion in the effluent from the cell
t - residence time in the cell

Prior experience with Donnan dialysis had shown that accumulated analytical error, uncertainty in solution flow rates, and uncertainty in volume measurements amounted to about 10%.

The number of sample sets to be taken during a single run depends upon the precision required for k, the rate constant. Since each sample set provided a value for C_o and a value for C, it was possible to calculate a value of k for each sample set using the cell residence time t determined by the feed flow rate in that particular run. The variability in k over a set of runs could then be determined. If one defined d as the half width of the desired confidence interval, then N, the number of sample sets required to give that precision, was

$$N = (ts^1/d^1)^2$$

where s^1 - relative standard devision of k
d^1 - half width of the desired confidence level expressed as a fraction of k
t - appropriate Students' t value for the desired significance level

For this study, a confidence interval half width of d = $\pm$0.1k had been set at a significance level of 0.05.

Table A.1 gives the data for the determination for three experimental runs in which 13 sample sets were used to determine k.

TABLE A.1. SAMPLE SIZE DETERMINATION FOR ESTIMATION OF k

Run	k	s	s^1	N*
A	0.893	0.133	0.149	11
B	0.751	0.087	0.116	8
C	1.329	0.101	0.076	5

* Rounded to next larger integar.

These three experimental runs were selected to cover the range of values for s which had been encountered on experimental runs early in the program. It therefore appeared that a sample size of 13 was adequate to provide values of k of acceptable precision for this study.

RATIONALE FOR SAMPLING

The membrane test system is shown in Figure 2 (p. 11). The system consisted of three dialysis cells in series, feed and recycle pumps, the necessary control valves and flow meters, and feed strip reservoirs. All pumps were equipped with variable speed drives. In operation, the feed and strip solutions were pumped into the system untilthe system was completely filled. The feed internal recycle pump and the strip recycle pump were started and run at 2 liters per minute to give a high flow rate through the cells, and the feed pump was started. The feed into and effluent from the system were adjusted to the flow rate to give the desired cell residence time. The system came to steady state in less than 2 hours when operated under these conditions. Samples were periodically taken of feed and cell effluent at the indicated sample points. A total of 13 sample sets was taken during an experimental run. Analysis of the samples provided the data rqeuired, along with cell residence time, to calculate the metal ion transport rate contant.

FACTORS AFFECTING SAMPLE RELIABILITY AND INTEGRITY

The sampling was straightforward. Samples were withdrawn from the system via hypodermic syringe at the septum-equipped sample points and placed directly into numbered acid-washed sample vials. The samples were diluted prior to analysis to bring the metal concentration into the linear response range for the particular metal in atomic absorption spectroscopy (AAS). Care in sampling, handling and dilution and in sample numbering avoided errors and produced reliable data.

SAMPLING APPROACH, LOCATION AND PROCEDURE

Feed and effluent samples were taken at the time the system reached steady-state (2 hours) and periodically (20-minute intervals) during the run. Samples were taken from a septum-equipped sample point between the feed reservoir and the feed pump. The effluent samples were taken from a septum-equipped sample point after the effluent flow meter. The system in operation depended upon an internal recycle to provide a high flow rate through the cells, and feed and effluent flow rates were then adjusted to give the desired cell residence time. In this operational mode, the system operated under steady-state conditions. The feed and sample points were positioned as described so they were external to the recycle system, and as a result, the taking of samples did not disturb the flows within the system and upset the steady-state conditions.

Sampling was accomplished by withdrawing the desired sample volume (5 mL) with a hypodermic syringe and placing the sample in a prenumbered acid-washed sample vial.

FLOW MEASUREMENTS

The feed flow rate, the feed recycle rate, and the strip solution recycle rate were measured with calibrated flow meters.

MATERIALS TO BE ANALYZED

The materials to be analyzed were aqueous solutions containing either cadmium, copper or zinc as their respective complex cyanide anions. The analyses were conducted by AAS. Cadmium, copper and zinc are analyzed by Methods 213.1, 220.1 and 280.1, respectively, as given in ''Methods for Chemical Analysis of Water and Wastewater'' (7).

DATA HANDLING PROCEDURES

A log book which contained forms for experimental runs was maintained. The run log recorded the metal species in the feed, feed concentration, feed flow rate, and feed recycle loop flow rate. Starting and completion times were recorded, as were sampling times and the corresponding sample numbers. An analytical data sheet was maintained for each run showing the analytical dilution factor, the analytical concentration found, and the actual concentration of the feed and effluent samples (analytical concentration found x dilution factor).

A separate calculation sheet showing the calculation of metal transport rate constants and material balance calculations was maintained in the log book.

QUALITY ASSURANCE/QUALITY CONTROL

The analytical chemistry quality control was achieved through the use of blind check standards at four concentration levels inserted into

run sample sets and by examination of the variability of the replicate feed sample analyses within each run.

Four check standards were randomly inserted into each sample set. The analyst was not aware which of the 30 individual samples (13 feed samples, 13 effluent samples, and 4 standards) were check standards thus ensuring equal treatment of the quality control standards and the run samples. The analytical data from each run were examined in two ways. The analytical value for the check standards was compared to the known value. Also, the relative standard deviation for the 13 replicate feed sample analyses was determined. Criteria for acceptance of the data set were agreement between the analytical value for each check standard and its true value within 5%, and a relative standard deviation for the feed sample analyses of 5% or less. Analysis of sample sets failing to meet either of these criteria were reanalyzed.

The above quality control procedure was in addition to those quality control procedures normally applied in the AAS laboratory.

The calibration procedure is patterned after ''Monitoring Industrial Wastewater,'' Section 8, Preparation of Standards and Calibration (8). Stock solutions of the metal(s) under study were prepared using high purity standards and reagents at concentrations of 100 mg of the metal per liter of water. These stock solutions were used to prepare the calibration standards.

A blank acid and calibration standard using the same type of acid as for sampling processing were prepared. The calibration standards covered the range of the samples where this was known or could be reasonably determined. The was aspirated folowed by the standards from lowest to highest concentration. A minimum of three aspirations (flame analysis) of each blank and standard was performed to establish that the calibration had not changed. Blans and standards were run not less than after every 20 samples and more frequently if in the judgement of the analyst a system change seemed likely. Flameless analysis generally required more frequent calibration (after every 10 to 15 samples).